"SYNTHESIS, STRUCTURAL DETERMINATION AND PHYSICO CHEMICAL STUDIES OF SOME ORDERED ORGANIC– INORGANIC HYBRID MESOPOROUS METALLOSILICATE SOLID CATALYSTS AND THEIR APPLICATIONS IN FINE CHEMICALS SYNTHESIS"

Pre-Synopsis

Submitted for the Degree of

DOCTOR OF PHILOSOPHY IN PHYSICS

To the

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Nanded

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(July-2022)

PRE SYNOPSIS

SYNTHESIS, STRUCTURAL DETERMINATION AND PHYSICO CHEMICAL STUDIES OF SOME ORDERED ORGANIC– INORGANIC HYBRID MESOPOROUS METALLOSILICATE SOLID CATALYSTS AND THEIR APPLICATIONS IN FINE CHEMICALS SYNTHESIS

1. INTRODUCTION:

Every part of the industries all over the humankind bring into being an hurtful squander like industrial, agricultural, electronic, several chemicals for instance HF, H_2SO_4, $HClO_4$ and H_3PO_4 which are used primarily in the areas of oil refining, petrochemicals etc are the dissipates[1,2] generating foremost challenges for instance severe health risks green problems and they have many disadvantages like difficulties in handling, plant corrosion, revival and environmentally safe disposal[3,4].

As well, in electric power generating plants, Coal fly ash is a byproduct from burning pulverized coal. During combustion, mineral impurities in the coal fuse in suspension and float out of the combustion chamber with the exhaust gases[5-8]. As the fused material rises, it cools and solidifies into spherical glassy particles called as fly ash. These fly ash particles create serious ecological problems and also disposal of such a massive quantity of ash has become a vital issue[9-12].

In the same way, Rice husk (RH) is an agricultural residue abundantly available in rice producing countries. Much of the husk produced from the processing of rice is either burnt or dumped as a waste openly, causing environmental and health crisis.

Taking this into an account we have decided to opt few industrial and agricultural wastes as a source to mechanize some industrially valuable and green mesoporous materials used for various chemical and physical applications. Thus the work would be a conversion of 'Waste to Wealth'.

2. REVIEW OF LITERATURE AND DEVELOPMENT IN THE SUBJECT:

Porous solids have extensive commercial applications as adsorbents, catalysts and catalyst supports due to their high surface areas. According to IUPAC definition porous materials may be divided into three types based on their pore dimensions:

Type and Pore Size (Å) Microporous : < 20 Mesoporous : 20-500 Macroporous : > 500

Well known microporous materials are zeolites and aluminophosphate molecular sieves which are inorganic composites having a crystalline three-dimensional framework woven with

tetrahedral atoms (T-atoms) like aluminium, silicon, phosphorous etc. bridged by oxygen atoms. These materials possess uniform channels or cavities circumscribed by rings of a definite number of T-atoms.

The exploitation of the architectural features of zeolites resulting in different acid sites and acid strengths, exchangeable ions, shape and size selective channels and pores etc. has been well established by now. Modification of the framework and extra-framework composition makes these materials useful for catalyzing organic reactions.

Till 1990 heterogeneous catalysis available with zeolites was restricted to the use of materials with pore sizes less than 20 Å and consequently the reactant molecules trapped and transformed inside them were also small. Thus the usefulness of the microporous molecular sieves in processing high molecular weight reactants of increasing importance was limited by their pore size (~ 7Å).

Hence there has been an ever-growing interest in expanding the pore sizes of the zeotype materials from the micropore region to mesopore region. The requirement of adsorbing larger molecules at the catalytic sites has led the development of molecular sieves with pore diameters larger than those of the traditional zeolites.

In order to preserve the remarkable catalytic properties of the zeolites while expanding their use to process bulkier molecules, new synthesis routes have been undertaken to increase their pore diameters.

This approach has led to the synthesis of ultra large pore molecular sieves. In 1982 Wilson and co-workers4 synthesized a novel crystalline, microporous aluminophosphate (AlPO4) material with a pore diameter of about 8 Å.

Later, in 1988, Davis et al. reported the synthesis of VPI-5, an AlPO4 molecular sieve with 18 tetrahedral atoms that could sorb molecules about 12 Å in size. Since then, microporous materials with pore openings containing 20 tetrahedral atoms have been synthesized (Table 1.1). They include cloverite , which is a gallophosphate and JDF-20, which is an AlPO4.

Recently a 14- membered ring (MR) unidirectional zeolite (UTD-1) was synthesized using a cobalt organometallic complex as the template. However, these materials lack the required thermal stability and catalytic activity because their frameworks are electrically neutral. Table 1.1 lists a few examples of zeolites and molecular sieves.

Table 1.1 Examples of zeolites/molecular sieves (Pore diameter < 20 Å)

Definition	Typical material	Ring size	Pore diameter (Å)	Ref.
Small pore	CaA	8	4.2	10
	SAPO-34	8	4.3	11
Medium pore	ZSM-48	10	5.3 × 5.6	12
	ZSM-5	10	5.3 × 5.6	13
			5.1 × 5.5	
Large pore	Faujasite	12	7.4	14
	$AlPO_4$-5	12	7.3	15
	ZSM-12	12	5.5 × 5.9	16
Ultralarge pore	Cloverite	20	6.0 × 13.2	6
	JDF-20	20	6.2 × 14.5	7
	VPI-5	18	12.1	5
	$AlPO_4$-8	14	7.9 × 8.7	17
	UTD-1	14	7.5 × 10	8

In current years, green perceptions and cost-effective thoughts have played a foremost and growing role of interest to find creative ways not only to reduce the natural wastes and industrial hazard to overcome the environmental pollution but also in redesigning commercially important processes so as to avoid the use of detrimental substances and the generation of venomous waste.

Among all the types of wastes, for the effective utilization of industrial wastes and agricultural wastes, we have opted these wastes produced after pyrolyzing coal and rice husk, sugar cane husk or pea nut husk at elevated temperature as the raw material and feed stock in our further studies rather than depleting them.

Coal Fly ash (CFA), Rice husk ash (RHA), Sugar cane husk (SCH) or Pea nut husk (PNH) are the low cost and readily available silica rich raw materials which can be used for the preparation of value added porous materials[13] like zeolite molecular sieves.

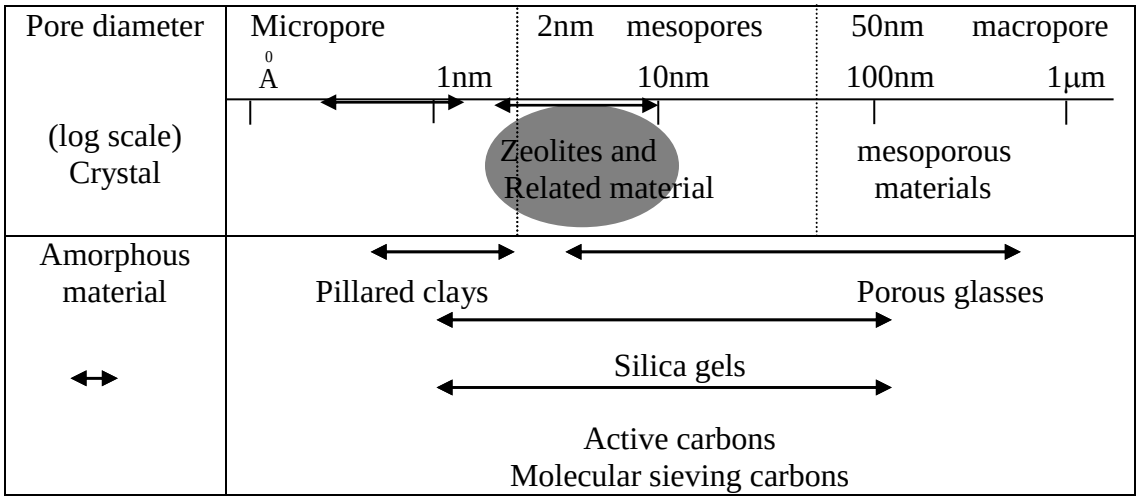
Converting these wastes into porous materials not only eliminates the disposal problems, but also turns an otherwise waste material into a marketable commodity as they have widespread applications in diversified fields.

The major components of CFA, RHA, SCH or PNH are silicon dioxide (SiO_2) and Aluminium trioxide (Al_2O_3), which are the essential reagents in the synthesis of zeolites (Shigemoto et.al., 1993; Chang and Shish,1998).

Synthetic zeolites obtained by reprocessing of CFA and RHA, sugar cane husk (SCH) or pea nut husk (PNH) have huge potential as a cost-effective, environmentally-friendly solution that can improve the efficiency of these materials as efficient heterogeneous catalysts, mainly as solid acids, as adsorbents, as molecular sieves in gas separation and purification[14-16] and in purification of contaminated waste water[17,19].

The low price and the additional ecological benefit of the production of zeolites from wastes increased their popularity and inspired growing interest among zeolite researchers and manufacturers worldwide.

Table – 1.2 : Classification of porous materials[20]



Zeolites have attracted widespread attention in scientific field as well as in industrial applications. It is a dynamic and rapidly growing field involving different branches of science like crystallography, theoretical physics, catalysis, inorganic, organic, physical, colloidal biochemistry, environmental science, mineralogy, geology and oceanography. Zeolites are fascinating class of solids, which have played key role in the vigorously growing impact on the world economy in the twentieth century.

'Zeolites' the aluminosilicate molecular sieves[13] are microporous materials which are inorganic composites. They have a crystalline structure woven with tetrahedral atoms like Al, P, Si etc bridged by oxygen atoms acquiring regular channels or cavities with an explicit number of tetrahedral atoms[21-24]. The crystallographic unit cell of the zeolites may be represented as:

$$M_{x/n}[(AlO_2)_x(SiO_2)y]\ zH_2O$$

Where,

M is a charge compensating cation with valency 'n'. The ratio 'x/y' may have any value ranging from zero to one. The number of water molecules, which can be reversibly adsorbed and desorbed in the zeolite pores, is represented by 'z'. Total number of tetrahedral sites in the unit cell of zeolites represented by x + y. In general, the ratio (y/x > 1) controls the morphology of zeolites and acidity to a lesser extent.

Moreover, zeolites and related molecular sieves have earned the reputation of 'green catalysts' due to several important environmental factors e.g. waste minimization, simple operation, easy work-up, regeneration and reuse of the catalysts for several times etc.

Nevertheless, these materials still suffer from inadequate thermal stability and limited catalytic activity because of the electrical neutrality of the framework. The main restriction of microporous zeolitic materials is their size constraints and therefore they are not suitable for catalytic transformations involving organic molecules having kinetic diameters above 0.75nm. Hence, there has been an ever-growing curiosity in escalating the pore sizes of the zeolitic resources from micro to mesoporous expanse.

Researchers have taken noteworthy pains to synthesize mesoporous silica materials. Actually, in 1990, Yanagisawa and co-workers,[14-25] described the preparation of mesoporous silicas with uniform pore size. However the pores in these materials were in general unevenly spaced and largely distributed in size. Thus, a gap has been bridged by the discovery of M41S family, which has opened up new possibilities for preparing catalysts with uniform pores in the mesoporous region.

In 1992, researchers at Mobil Research and Development Corporation reported the synthesis of a new family of silicate/aluminosilicate mesoporous molecular sieves (M41S) with exceptionally large and uniform pore structures.[26-30] These materials possess well-defined mesopores whose diameters can be tailored in the range of $20A^0$-$100A^0$ with high surface area (>$900m^2/g$) and precise tuning of the pores are among the desirable properties of these materials.

The important members of the mesoporous family are MCM-41, MCM-48 MCM-50 and SBA-15, SBA-16. MCM-41 possess honeycomb arrays of non intersecting uniformly sized channels

depending on the template used, the addition of auxiliary organics and the synthesis parameters like synthesis time, synthesis temperature or post synthesis treatments.

The main characteristics of MCM-41, 48 materials are their better thermal stability, large surface area and narrow pore size distribution. MCM-41, 48 are structurally stable towards thermal treatment, hydrothermal treatment with steam at mild conditions, mechanical grinding and also towards acid treatment at mild condition. MCM-41, 48 has high potential for practical use as an adsorbent or a mesoporous support for depositing active catalyst components, particularly useful in the synthesis of fine chemicals involving bulky molecules.

The wide spectrum of pore diameter makes these materials readily accessible to large molecules, and has major significance in their processing. The most outstanding feature of the preparation of the mesoporous materials is the role of the templating agents. The formation of mesoporous materials with a variety of crystallographically well-defined frameworks have been made possible via a generalized "liquid-crystal templating" (LCT) mechanism.

The large regular pore structure of mesoporous materials make them suitable for liquid-phase acidic and basic catalysis by enabling rapid diffusion of reactants and products through the pores, thus minimizing consecutive reactions.

Different synthesis strategies have been proposed and successfully used to prepare mesoporous molecular sieves, hydrothermaly by mixing surfactants, silica, and/or silica-alumina source to form a gel while maintaining the mixture at a temperature between 70 and 160^0C for a fixed period of time.

Table - 2 : Types of materials

Surfactant/Silica	**Typical phase**
< 1.0	Hexagonal phase (MCM-41)
= 1.0 - 1.5	Cubic phases (MCM-48)
= 1.2 - 2.0	Thermally unstable materials
= 2.0	Cubic octamer [(CTMA)SiO_2.]

The product obtained after crystallization is filtered, washed with distilled water, dried at ambient temperature. To get mesoporous silicate/aluminosilicate network, surfactant molecules are removed by calcination. The structure and pore diameter of mesoporous materials can be altered by varying the surfactant/SiO_2 ratio. It has been found that as the surfactant/silica molar ratio increased, the siliceous products obtained could be grouped into four categories:

A number of models such as Liquid Crystal Templating (LCT) Mechanism, Silicate Rod Assembly, Charge Density Matching and Folding Sheets etc. have been proposed in order to explain the mechanism of formation of mesoporous materials by various synthesis routes.

All these models are based on the presence and the role of surfactants in solution to guide the formation of inorganic mesostructures. In solution, surfactants having two parts within the same molecule (hydrophilic head group and long chain hydrophobic tail group) will aggregate and self organize in such a way as to minimize contact between the incompatible ends.

The type of interaction between the surfactant and the inorganic precursor under different synthesis conditions needs careful attention and is a subject of much discussion.

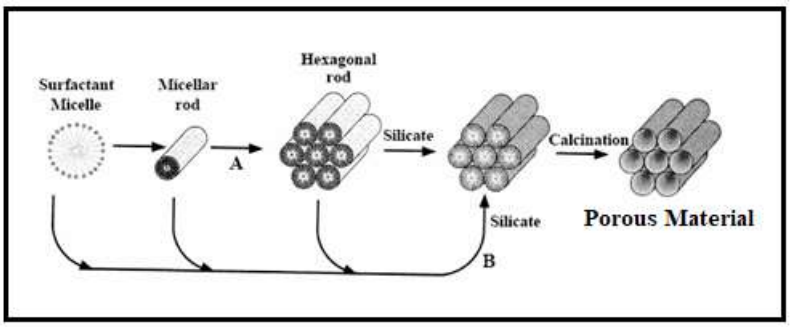


Fig.1: Liquid crystal templating mechanism proposed for the formation of Mesoporous Materials : (A) liquid crystal phase initiated and (B) silicate anion initated.

In order to generate potential catalytic activities, the incorporation of heteroatoms into the inert framework or walls of pure siliceous mesoporous materials is an important route to modify the nature of the framework and make them catalytically active.

In general, it is observed that the incorporation of tetrahedrally coordinated Aluminium on the walls during the synthesis decreases the order in the material and the degree of incorporation depends on the Aluminium precursor and method of preparation.

The incorporation of trivalent metal ions such as Al, B, Ga, Fe etc. in the walls of silica network mesostructure produces framework negative charges that can be compensated by protons providing acid sites and therefore, such materials are important from the point of view of acid catalysis.

The incorporation of transition metal elements such as Ti, V, Cr, Mn, Fe, etc. is also important to prepare mesoporous catalysts with redox catalytic properties.

The incorporation of alkaly metal elements such as Na, K, Rb and Cs are also important to prepare mesoporous catalysts with basic catalytic properties.

MESOPOROUS SILICATES AS SUPPORT/HOST:

Immobilization of Metals/Metal Complexes in Mesoporous Silicates:

The post-synthesis immobilization of metals and organometallic complexes on the surface of mesoporous silicates allows the preparation of multifunctional molecular sieves with desired catalytic properties. Mesoporosity and very high surface area of mesoporous materials have been largely used for the immobilization of different metals as well as bulky organometallic complexes. The processes for metal immobilization include wet impregnation, vapor deposition, treatment with $(NH_4)_2MF_6$ (M = Si4+, Ti4+, etc.) and metal alkoxides, ion exchange with metal salts etc.

The immobilization of metal complex is mostly done by ion exchange followed by the complexation with ligand and also by direct incorporation of the metal complex in the mesoporous hexagonal channels.

The advantages of inorganic-organic hybrid materials arise from the fact that inorganic components can provide mechanical, thermal or structural stability, while the organic features are more readily modified for specific applications in catalysis, separation or sensing.

The presence of large amount of silanol groups [$(\text{-O-})_3\text{SiOH}$] in mesoporous materials attracted the researchers primarily for anchoring the organic functional groups using the concept of organic functionalization in silica gel and then those organic functional groups or ligands were used for anchoring different types of metal complexes with or without modification of the parent functional groups.

Organically functionalized mesoporous silicas were prepared conveniently at room temperature or at higher temperature by the co-condensation of tetraalkoxysilane ($Si(OR)_4$) and organosiloxanes ($R1\square Si(OR)_3$) in the presence of surfactant (template) and auxiliary chemicals. Thus, a variety of inorganic -organic hybrid materials, where the organic functional groups are attached covalently with the silica surface of porous materials through Si-C bonds, are very important for their various potential applications. An acidic solvent extraction technique is generally used to remove the surfactant from the product to yield an organofunctionalized ordered porous silica material.

Organo functional groups were also introduced to the pore surface of mesoporous silica as the terminal groups for organic monolayers by post synthesis modification. The treatment of mesoporous silica with organosiloxane precursors produces hybrid inorganic-organic materials by hydrolysis and finally condensation of organosiloxane groups.

Although the organic functional groups have been introduced into mesoporous silica in both ways, *in situ* and post synthetic methods, organometallic complexes attached covalently to the pore surface are introduced only by post synthesis modifications.

Extensive research efforts have been undertaken to control the crystal size, pore dimensions and pore sizes. The control of crystal size and pore dimensions are also important factors, particularly for MCM-41, 48 with unidirectional channels. High quality hexagonal mesoporous materials of good thermal stability and smaller crystal sizes were obtained by heating precursor gels in the microwave at 150ºC for 1 h or even less.

The disordered mesoporous material, KIT-1, interconnected in a three-dimensional and fully disordered way is also of interest from the catalytic point of view. One of the most interesting and useful features of M41S family is the flexibility to synthesize these materials with different pore diameters (2-10 nm). This can be achieved in three different ways:

i) by varying the chain length of hydrophobic alkyl group (8 to 22 carbon atoms) in the surfactant molecules,[25]

ii) by adding organic swelling agents such as 1,3,5-trimethylbenzene,[26] alkanes of different chain length,[26] etc. which will increase the micellar size by solvation of the added hydrophobic molecules in the hydrophobic region of the micelles

iii) by adjusting the composition of the gel and the crystallization variables. In a different approach, Sun and Ying were able to control pore sizes between 0.5-2 nm by the use of short-chain alkylamines as supramolecular templates, allowing for systematic bridging of the mesoporous and microporous regimes.

The ligand-assisted templating (LAT) technique was further modified by them to produce microporous Nb-TMS6 with the use of dialkylamines.

The morphology of originally obtained mesoporous materials consists of aggregates and loose agglomerates of small particles. However, for many applications in catalysis, chemical sensoring or as optical devices, well-defined morphologies are required.

The research has been focused to obtain thin films, fibers, spheres and monoliths. Huo et al. and Yang et al. have used acid medium ($S^+X^-I^+$) for the preparation of a large variety of differently curved and highly interesting morphologies.

Thin films have been prepared at the air/water and oil/water interface as free-standing films, on both the mica and the graphite surfaces and by using dip- or spin-coating techniques. While, the preparations of fiber morphologies were carried out in oil-in-water emulsions and in aqueous phase under acidic ($S^+X^-I^+$) conditions, the syntheses of hollow as well as hard spheres of mesoporous silicas were carried out by emulsion biphase chemistry.

Monolithic periodic mesoporous silicas prepared by different systems using ionic and non-ionic surfactants are also very important for several applications. An interesting morphology of 'tubules-within-a-tubule' hierachiral order has been reported by Lin and Mou.

PHYSICO-CHEMICAL CHARACTERIZATION:

Various techniques are used to characterize mesoporous molecular sieves. Among them,

1. X-ray powder diffraction for Phase identification (Qualitative analysis), Quantitative phase analysis, Determination of crystallinity, Crystallite size
2. Adsorption measurements,
3. Scanning electron microscopy (SEM) are the indispensable ones to recognize the configuration of the mesoporous molecular sieves
4. Diffuse reflectance U.V. spectroscopy and Infrared spectroscopy have also been applied to obtain additional structural information about molecular sieves.
5. TG-DTA is performed to examine the thermal stability of the synthesized material.
6. Surface area (BET) and Pore size distributions (BJH) and pore volume and pore size distribution by the BJH Method.
7. Fourier transforms infrared (FTIR) spectroscopy
8. Atomic absorption spectroscopy (AAS)
9. TPD of ammonia
10. Energy Dispersive Analysis of X-ray (EDAX)
11. Gas Chromatography Mass Spectrometry (GC-MS)
12. X-ray fluorescence Spectroscopy (XRF)

APPLICATIONS OF MESOPOROUS MATERIALS:

In waste water treatment:

Mesoporous materials have a great potential as effective sorbent materials for a large number of water treatment applications such as water softening, removal of heavy metals (from natural waters, acid mine drainages, industrial wastewater), phosphates, phenols removal, removal of dissolved organic and inorganic compounds, separation of solid impurities, radioactive wastewater purification and many others.

Waste water treatment methods:

Water to be supplied for public use must be potable i.e., satisfactory for drinking and useful for agriculture purposes from the standpoint of its chemical, physical and biological characteristics. Water from natural, industrial, municipal or agricultural origin may contain variety of suspended, dissolved, colloidal or emulsified organic and inorganic impurities, some of which could be successfully separated out, using special class of inorganic compounds, called "Mesoporous zeolites".

Some of the common treatment processes for purification of waste water are:

* Chemical precipitation,
* Coagulation–precipitation,
* Membrane filtration,
* Reverse osmosis and
* Adsorption and ion exchange

Among the various types of purification methods, ion exchange methodology is the cost effective methodology and is one of the most well-developed, common, and effective treatment methods for treatment of contaminated water.

Mesoporous materials are the well known for its ion exchange capacity. Ion exchange method has been proved to be very effective for removing contaminants from water and increase the water quality.

As Ion Conducting and Dielectric material:

Mesoporous materials are ion conducting and dielectric in nature. A material is classified as dielectric if it has the ability to store energy when an external electric field is applied. The complex electrical properties such as (dc and dielectrical properties) have been the subject of intense studies. These properties of the zeolites are mainly related to the chemical composition, Si/Al ratio, the type of exchangeable cations, degree of exchangeable cations, the state of hydration and temperature. Compared with other ionic crystalline solids, zeolites have a high electric conductivity.

This conductivity results from the great mobility of exchangeable cations. Thus MCM-41, 48 can be regarded as weak electrolytes. Their conductivity is of the cations between close sites. Dc conductivity and dielectric properties of pre and post modified forms of MCM-41 were reported.

Catalytic Applications and prospect :

Solid acid-base catalysis is one of the economically and ecologically important fields in catalysis. Due to their non-corrosive and environmentally friendly nature, with a fewer disposal problems, easy separation along with their higher activity, selectivity and longer catalyst life lead to the replacement of homogeneous catalysts with the heterogeneous ones and thus becoming even more important in chemical and biological industries. Among the heterogeneous catalysts, mesoporous materials played a vital role and as per the survey large number of reactions are catalyzed by MCM-41,48.

MCM-41,48 can be used as catalysts for many principal reactions in organic chemistry. MCM-41,48-catalyzed reactions include electrophilic and nucleophilic substitution reactions, addition and elimination reactions, isomerization and rearrangement reactions oxidation and condensation reactions.

The unique physical properties (e.g. high specific surface area, large pore size etc.) of MCM-41,48 have made these materials highly desirable hosts for the fixation of large active complexes. Due to large void space the diffusional restrictions of reactants or products are absent and therefore, these materials are quite suitable for catalytic applications involving bulky molecules.

Other Applications:

As far as crystalline porous materials are concerned, mesoporous molecular sieves will continue to be used in the now – practiced, not only because of their important industrial applications as adsorbents, ion-exchange and catalysts but also because of their potential applications as hosts for a variety of technologically advanced materials such as semiconductor

clusters, molecular wires with tailored electronic and optical properties, enzyme mimicking organic complexes etc.

New directions in the past 20 years include environmental and biopharmaceutical applications which have only recently received attention.

Future applications of MCM-41,48 in space could also be the use as catalysts for sugar and carbohydrate fractionating as an effective energy conditioning medium for food in space. Latest application of micro or mesoporous zeolite in space by NASA is the removal of gas components under ultra clean room conditions in satellite systems and the Hubbell telescope, reduce the outgasing rate inside instruments and absorb molecules without producing additional particles by themselves.

Environmentally benign MCM-41,48 catalysts have wide potential as solid acids in many commercial processes. Four interrelated forces are driving clean technologies in industrialized countries:

* Regulatory pressures to decrease the output of waste streams and by products.
* The need to remain cost competitive with third world manufactures unencumbered by stringent environmental regulations.
* Social demands for a clean environment and sustainable production methods and
* Increased knowledge of the cause, effects, and dispersion of pollution.

It is widely recognized that the gains made by the current generation of environmental technologies are being offset by population growth. Consequently, many new and creative pollution prevention and abatement methods are required. The unique properties and selectivities of MCM-41,48 zeolites can provide effective environmental solutions by minimizing the output of pollutants and by secondary treatment of effluents produced.

APPLICATIONS AND FORECASTS:

The high surface area and large pore size of MCM-41,48 favour high dispersion of the active species and provide easy convenience to large feed stock molecules making it an attractive catalyst. Other potential applications for these novel materials are in sorption, separations, polymer

chemistry etc. To date several mesoporous metallo-silicates with significant catalytic properties have been synthesized. Some of the reactions studied on different metallosilicate molecular sieves are listed in Table 1.3.

Table 1.3 : Reactions studied on mesoporous metallosilicate molecular sieves

No.	Catalyst	Reaction
1	Al-MCM-41,48	Alkylation of 2,4-di-ter. butyl phenol with cinnamyl alcohol
2	Al-MCM-41,48	Cumene hydrocracking
3	Al-MCM-41,48	Conversion of plastic wastes into hydrocarbons with low aromatic content
4	Ni-MCM-41,48 and Mo-MCM-41,48	Hydrode-nitrogenation, hydrodesulfurization and hydrocracking of gas oil
5	Ti-MCM-41,48 and Ti-HMS	Epoxidation of 1-hexene using H_2O_2, epoxidation of norbornene using TBHP as oxidant
6	Ti-MCM-41,48 Ti-HMS and V-HMS	Oxidation of phenol and 2,6-di-tert-butyl phenol using H_2O_2 as oxidant
7	Ti-MS and Zr-MS	Oxidation of aniline to azoxibenzene, epoxidation of cyclohexene, norbornene and oxidation of 2,6- di-tert-butyl phenol using H_2O_2 as oxidant
8	V-MCM-41,48	Oxidation of cyclodecane and 1-naphthol using H_2O_2 as oxidant
9	Cr-MCM-41,48	Oxidation of phenol, 1-naphthol and aniline using H_2O_2 as oxidant
10	Mn-MCM-41,48	Conversion of propene to CO_2
11	Na-MCM-41,48 Cs-MCM-41,48 and Al-MCM-41,48	Knoevenagel condensation of benzaldehyde and salicylaldehyde with cyanoacetate
12	Cs-MCM-41,48	Addition of diethyl malonate to neopentyl glycol
13	Cu- and Fephthalocyanine -MCM-41,48	Oxidation of n-hexane using TBHP as oxidant
14	Pt-MCM-41,48	Oxidation of carbon monoxide

3. OBJECTIVES OF THE RESEARCH / PROPOSED HYPOTHESIS

The objectives of the present work are:

1. Extraction of silica from CFA, RHA, CSH and PNH
2. To synthesize MCM-41, 48 using silica extracted from CFA and RHA, CSH, PNH and to optimize the synthesis procedures.
3. To study the kinetics of crystallization on synthesized materials such as

- Effect of crystallization time
- Effect of Temperature
- Effect of P^H
- Effect of calcination period
- Effect of NaOH

4. To synthesize MCM-41 and to optimize the synthesis procedures.
5. To synthesize Al-MCM-41, Sn-MCM-41and Zr-MCM-41 (metal incorporated MCM-41).
6. To study the effect of templating agents (surfactants) on the physico-chemical properties and morphology of MCM-41 and metal incorporated MCM-41 samples.
7. To characterize the synthesized samples in detail using various techniques and tools such as elemental analysis, XRD, TGA/DTA, N2-adsorption measurements, electron microscopy (TEM/SEM), pyridine-TPD, UV-visible, FT-IR, MAS NMR, ESR and microscopy (TEM/SEM), pyridine-TPD, UV-visible, FT-IR, MAS NMR, ESR and Mössbauer spectroscopic methods.
8. To study the catalytic activity of H-MCM-41 in reactions such as the Beckmann rearrangement of cyclohexanone oxime, alkylation of benzene with long chain olefins and hydroisomerization of n-hexane over Pt-H-MCM-41.
9. To evaluate the catalytic activities of Sn-MCM-41 and Zr-MCM-41 samples in various oxidation reactions.
10. Post Modification of synthesized materials (metal incorporated synthesized materials).
11. To characterize the synthesized samples and modified samples of synthesized materials in detail using various techniques and tools such as elemental analysis, XRD, N_2-adsorption measurements, electron microscopy (SEM), TGA/DTA, ammonia-TPD, UV-visible, FT-IR, etc.
12. To study the effect on the adsorptive behavior of pre and post modified synthesized materials
13. To study the catalytic activity of synthesized materials in diverse reactions.
14. To deal with an account of conductivity behavior of selected samples.

4. METHODOLOGY TO BE ADOPTED:

Hydrothermal synthesis of mesoporous molecular sieves was carried out in hydrothermal reactor at autogenous pressure under stirring conditions. However an ion exchange method will be adopted for post modification and to perform some heterogeneous chemical reactions and also to study some 'Freundlich adsorption' applications

5. IMPORTANCE OF STUDY:

Synthesis of mesoporous materials from chemical sources of silica and alumina is expensive therefore; their use in environmental remediation is restricted due to prohibitive costs, which can be overcome by seeking cheaper raw materials for their synthesis. These include clay minerals, rice husk ash, coal fly ash, etc.

Therefore, our research endeavors the use of no-cost raw materials such as industrial waste CFA collected from the Thermal Power Stations and agro waste rice husk from the rice mills. The reasons for choosing these sources for our further investigations are:

1) They add value; reduce the cost and creates effective utilization to protect the environment.

2) Their potential application in synthesis of highly useful porous materials.

3) Their potential application in water purification technology, as industrial catalyst, supporting materials, exchanger, molecular sieves etc.

It was therefore, thought desirable to extract silica from silica rich CFA, RHA, CSH and PNH. Further this extracted silica was used as a starting material for the synthesis of mesoporous molecular sieves such as MCM-41, 48 and their applications were also studied.

However, the amorphous framework structure and the lack of active centers in the pure silica mesoporous material have restricted their direct application.

In order to impart the catalytic and adsorptive activity to the chemically inert mesoporous silicate framework, substitution of Si^{4+} ions by other heteroatom in the prepared materials has been endeavored.

Modification of these materials with heteroatom such as Al, Cs etc. has resulted in materials with considerable enhancement in catalytic activity of reactions of bulky molecules and the adsorption activity.

It is evident from the literature survey on mesoporous molecular sieves, that these materials have opened new opportunities in the field of catalysis, adsorption etc. The objective of this study is to prepare optimized mesoporous, functional materials and to explore their application in selective catalytic transformation of organic molecules, at ambient conditions, in a range of reactions. The formation, purity, characteristics and reaction mechanism have been investigated using a range of physicochemical techniques.

The framework composition can easily be modified by incorporation of monovalent and trivalent elements, thus providing solids with potential applications in acid or basic reactions. Metal species are usually highly dispersed in the silica framework making the otherwise chemically inert framework catalytically active.

In the present work metal ion containing mesoporous molecular sieves will be synthesized from CFA, RHA, CSH and PNH etc. Synthesized materials will be characterized and catalytically evaluated in various condensation reactions also in studying their adsorptive and conductivity behavior.

The pre and post modified molecular sieves will be examined as the value added products as they are noncorrosive, eco- friendly, easy to handle and reusable. Materials can also be utilized in medicinal drug formation and mechanism.

It is evident from the literature survey on mesoporous molecular sieves, that these materials have opened new opportunities in the field of catalysis. The framework composition can easily be modified by incorporation of trivalent and tetravalent elements, thus providing solids with potential applications in acid or redox reactions.

Metal species are usually highly dispersed in the silica framework making the otherwise chemically inert framework catalytically active. In the present work aluminium, tin and zirconium containing mesoporous molecular sieves MCM-41 have been synthesized, characterized and catalytically evaluated in few reactions.

Solid acid catalysts have been widely used in chemical industries, as they are noncorrosive, eco-friendly, easy to handle and reusable. In the present investigation, Pt loaded H-Al-MCM-41 molecular sieves have been catalytically evaluated in the hydroisomerization of n-hexane which is an important process in the petroleum refining industry for obtaining high octane gasoline blendstocks, and which has been investigated by earlier workers on molecular sieves such as Pt-Y, Pt-beta, Pt-mordenite and Pt-ETS-10.

Liquid phase Beckmann rearrangement of cyclohexanone oxime using methanol and hexanol as solvents to prepare e-caprolactam, which is the monomer of nylon-6 has been studied by Dai et al. They reported that the protonic form of mesoporous molecular sieves possessed high activity for the rearrangement.

A comparative study of this reaction will be made over Si-MCM-41, H-Al-MCM-41 and Pt-H-Al-MCM-41. Linear alkyl benzenes (LAB) are important in the manufacture of detergents. The alkylation of benzene with long chain alkenes has been reported over heteropolyacids, clays, pillared clays and ZSM-12 and a number of medium and wide pore zeolites.

In the present thesis a comparative study of the alkylation of benzene with long chain olefins over mesoporous Al-MCM-41, ReY and amorphous silica-alumina catalysts is being studied. The incorporation of Ti and V into MCM-41 has been extensively studied and shown to result in active catalysts for the oxidation of larger molecules.

Systematic studies on the incorporation and characterization of Fe, Cr and Mn in MCM-41 have been reported. But, limited reports are available on the synthesis, characterization and catalytic evaluation of zirconium containing mesoporous molecular sieves.

Hence it was decided to study in detail the incorporation of zirconium in MCM-41. Substitution of aluminium by tin in the faujasites, mordenites and ZSM-5 by post synthesisor by hydrothermal crystallization and of silicon in Sn-silicalite-1 and Sn-silicalite-2 is known.

Sn-silicalite-1 and Sn-silicalite-2 (medium pore zeolites) are catalytically active in the hydroxylation of small molecules such as phenol and cresol. So far there are no reports regarding the isomorphous substitution of tin in MCM-41 structure. These materials are found to be useful for the oxidation of large molecules such as 1-naphthol and norbornene

6. PROPOSED WORK PLAN:

The present work aimed to synthesize silica based mesoporous materials from industrial and agricultural wastes and their applications in various physical and chemical perspectives is broadly elaborated in three consecutive years is depicted as follows:

First Year:-

1. To collect the references in relevant field.
2. To attend the seminars/ conferences/ workshops on relevant topic.

3. To study the various papers and finalize one of the schemes of synthesis such as hydrothermal or in *situ* method.

Second Year:-

1. To study the existing and new techniques which will be applied in our research work?
2. Collection of industrial and agricultural wastes such as coal fly ash, rise husk ash or pea nut husk or cane sugar husk followed by their calcinations so as to remove the carbonius and magnetic material by magnetic stirring.
3. Screening of this calcined and demagnetized raw material to obtain fine residue for our further investigation.
4. Some characterization such as XRD, FTIR, SEM and EDAX will be taken to find out the percentage of silica and other components.
5. Rich silica raw material will be choosed for our further synthesis of mesoporous silicious material.
6. Silica will be leached by the leaching process from sodium hydroxide which will be a supernatant for the synthesis purpose.
7. Keeping the aim of synthesizing MCM-41, 48 from among the various mesoporous materials.
8. Synthesis process will be optimized by studying the effect of synthesis temperature, calcinations temperature, pH, time, effect of NaOH, reusability, etc.
9. To optimize the superior industrially optimum material, it is to be characterized by series of large characterization such as XRD, FTIR, EDAX, SEM, TEM, TGA and DTA, UV, etc.
10. Once the material is optimized, to enhance its physical and chemical activity post modification with some metal ion will be followed to prepare M-MCM 41, 48.
11. Post modified synthesized material will be used in some physical and chemical applications.

Third Year:-

1. To publish the work in reputed peer reviewed international journals.
2. To compile the data for thesis writing and eventually the thesis will be submitted to the concerned authority.

7. REFERENCES:

1. Toxic Air : The Case for Cleaning Up Coal-fired Power Plants (Report). *American Lung Association*. March 2011. p. Retrieved **(2012-03-09)**.
2. "Benzene Exposure on a Crude Oil Production Vessel -- KIRKELEIT et al. 50 (2): 123 -- Annals of Occupational Hygiene". *annhyg.oxfordjournals.org. Retrieved* **(2010-06-07)**.
3. "Pennsylvania, New Jersey – Philadelphia Toxic Tort / Chemical Injury Attorneys". *Retrieved* **(2010-05-04)**.
4. "Environmental impacts of coal power: air pollution". Union of Concerned Scientists. *Retrieved* **(2012-03-09)**.
5. "Environmental Impacts of Coal Mining". World Coal Institute. *Retrieved* **(2008-10-22)**.
6. D.J. Fauth, E.A. Frommell, J.S. Hoffman, R.P. Reasbeck, H.W. Pennline, Fuel Process. Technol. 86 (14–15) (2015) 1503–1521.
7. APGTF, Cleaner Fossil Power Generation in the 21st Century: Maintaining a Leading Role, UK, (2011).
8. C. Xu, N. Hedin, Mater. Today 17 (8) (2014) 397–403. [15] Y. Zheng, R. Zou, Y. Zhao, Adv. Mater. 28 (15) (2016) 2855–2873.
9. T. Sakpal, A. Kumar, S.P. Kamble, R. Kumar, Indian J. Chem. Sect. 51 (9) (2012) 1214–1222. [17] W.J. Son, J.S. Choi, W.S. Ahn, Microporous Mesoporous Mater. 113 (2008) 31–40.
10. A. Samanta, A. Zhao, G.K.H. Shimizu, R. Gupta, Ind. Eng. Chem. Res. 51 (2012) 1438–1463.
11. J. Wang, L. Huang, R. Yang, Z. Zhang, J. Wu, J. Gao, Q. Wang, D. O'Hare, Z. Zhong, Energy Environ. Sci. 7 (2014) 3478–3518.
12. K. Li, J. Jiang, F. Yan, S. Tian, X. Chen, Appl. Energy 136 (2014) 750–755.
13. K. Li, J. Jiang, S. Tian, F. Yan, X. Chen, R. Soc. Chem. 3 (2015) 2166–2175.
14. W. Zhang, H. Liu, C.G. Sun, T.C. Drage, C.E. Snape, Chem. Eng. J. 251 (2014) 293–303.
15. N. Sun, Z. Tang, W. Wei, C.E. Snape, Y. Sun, Solid adsorbents for CO2 capture with low energy penalties leading to integrated low carbon energy solutions, Front. Energy Res. 3 (2015) Article 9.
16. Liou, T.-H. A green route to preparation of MCM-41 silicas with well-ordered mesostructure controlled in acidic and alkaline environments. *Chem. Eng. J.* **2011**, *171*, 1458–1468.
17. Deekamwong, K.; Kaiyasuan, C.; Jitcharoen, J.; Wittayakun, J. Influence of gel composition and microwave-assisted hydrothermal time in MCM-41 synthesis. *Mater. Chem. Phys.* **2017**, *201*, 384–390.
18. Cheng, C.-F.; Zhou, W.; Ho Park, D.; Klinowski, J.; Hargreaves, M.; Gladden, L.F. Controlling the channel diameter of the mesoporous molecular sieve MCM-41. *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 359–363.
19. McManamon, C.; Burke, A.M.; Holmes, J.D.; Morris, M.A. Amine-functionalised SBA-15 of tailored pore size for heavy metal adsorption. *J. Colloid Interface Sci.* **2012**, *369*, 330–337.
20. Da'na, E. Adsorption of heavy metals on functionalized-mesoporous silica: A review. *Microporous Mesoporous Mater.* **2017**, *247*, 145–157.

21. Glotov, A.; Vutolkina, A.; Pimerzin, A.; Nedolivko, V.; Zasypalov, G.; Stytsenko, V.; Karakhanov, E.; Vinokurov, V. Ruthenium Catalysts Templated on Mesoporous MCM-41 Type Silica and Natural Clay Nanotubes for Hydrogenation of Benzene to Cyclohexane. *Catalysts* **2020**, *10*, 537.
22. Dong, C.; Deng, X.; Guo, X.; Wang, B.; Ye, X.; Fan, J.; Zhu, C.; Fan, F.; Qing, B. Synthesis of potassium metal ferrocyanide/Al-MCM-41 with fast and selective adsorption of cesium. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *613*, 126107.
23. Subsadsana, M.; Kham-or, P.; Sangdara, P.; Suwannasom, P.; Ruangviriyachai, C. Synthesis and catalytic performance of bimetallic NiMo- and NiW-ZSM-5/MCM-41 composites for production of liquid biofuels. *J. Fuel Chem. Technol.* **2017**, *45*, 805–816.
24. Sohrabnezhad, S.; Daraie Mooshangaie, S. In situ fabrication of n-type Ag/AgBr nanoparticles in MCM-41 with rice husk (RH/MCM-41) composite for the removal of Eriochrome Black-T. *Mater. Sci. Eng. B* **2019**, *240*, 16–22.
25. Liu, J.; Wei, X.; Xue, J.; Su, H. Preparation and adsorption properties of mesoporous material PS-MCM-41 with low-silicon content peanut shell ash as silicon source. *Mater. Chem. Phys.* **2020**, *241*, 122355.
26. Ma, Y.; Chen, H.; Shi, Y.; Yuan, S. Low cost synthesis of mesoporous molecular sieve MCM-41 from wheat straw ash using CTAB as surfactant. *Mater. Res. Bull.* **2016**, *77*, 258–264.
27. Li, C.-C.; Qiao, X.-C.; Yu, J.-G. Large surface area MCM-41 prepared from acid leaching residue of coal gasification slag. *Mater. Lett.* **2016**, *167*, 246–249.
28. Cheng, S.-Y.; Liu, Y.-Z.; Qi, G.-S. Experimental study of CO_2 capture enhanced by coal fly ash-synthesized NH2-MCM-41 coupled with high gravity technology. *Chem. Eng. J.* **2020**, *400*, 125946.
29. Yao, Z.T.; Ji, X.S.; Sarker, P.K.; Tang, J.H.; Ge, L.Q.; Xia, M.S.; Xi, Y.Q. A comprehensive review on the applications of coal fly ash. *Earth-Sci. Rev.* **2015**, *141*, 105–121.
30. Zanoletti, A.; Federici, S.; Borgese, L.; Bergese, P.; Ferroni, M.; Depero, L.E.; Bontempi, E. Embodied energy as key parameter for sustainable materials selection: The case of reusing coal fly ash for removing anionic surfactants. *J. Clean. Prod.* **2017**, *141*, 230–236.

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